UNIVERSITY OF TECHNOLOGY SYDNEY

DOCTORAL THESIS

Optical Transport of Pseudo-Random Coatings

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Declaration of Authorship

I, Marc A. GALÍ LABARIAS, declare that this thesis titled, "Optical Transport of Pseudo-Random Coatings" and the work presented in it are my own. I confirm that:

- This work was done wholly or mainly while in candidature for a research degree at this University.
- Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated.
- Where I have consulted the published work of others, this is always clearly attributed.
- Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work.
- I have acknowledged all main sources of help.
- Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself.
- This research is supported by an Australian Government Research Training Program.

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"All truths are easy to understand once they are discovered; the point is to discover them."

Galileo Galilei

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Abstract

Science
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Optical Transport of Pseudo-Random Coatings

by Marc A. GALÍ LABARIAS

Coatings are widely used to improve the optical performance of surfaces exposed in the built environment, technological devices, and consumer goods. In the last decades the improvement of techniques to create structured coatings has hugely increased the range of properties that can be achieved by such systems. Unfortunately, the theoretical techniques to model the complex and often pseudo-random nature of structured coatings are not yet fully adequate. In this thesis I will address this problem. Specifically, I will develop improved techniques that can be used on different kinds of coatings: mesoporous metals, random two-phase structures, heterogeneous matrices and rough surfaces.

First, I will consider silver mesoporous sponges. These are both random and isotropic, and are readily synthesized in the laboratory in various physical densities. Therefore they provide a useful platform on which to begin developing computational strategies. I will analyse these structures using an *effective medium approximation* based on their far-field response. Mesoporous metals offer a very distinct optical response compared to their constitutive bulk metal. In particular, the topology of such structures creates metal systems with low plasmon response but with high conductivity thanks to their percolated metal *filaments*. These characteristics make them suitable for many applications, for example as highly absorptive optical coatings.

Next, I will introduce the concept of anisotropy into the coating structure by analysing columnar morphologies obtained using physical vapour deposition. These kind of coatings offer some degree of order caused by shadowing effects, and a degree of randomness due to the statistical roughening present when depositing such structures. The most important structural dependence is the plane perpendicular to the growth direction, hence in this work I will analyse them as two-dimensional structures. I will obtain the effective permittivity and optimal bounds (which I will call *leaf bounds*) by expanding the averaged polarization field in a power series on the susceptibility. To

do this we developed a method that relies on a Monte Carlo algorithm to efficiently obtain higher orders of this series expansion. Therefore, this new methodology permits the study of higher order micro-structural parameters. In this thesis I will analyse up to fourth order effects. For anisotropic coatings, the depolarization of the Gaussian random fields studied is related to the depolarization factors of an ellipsoid with the same anisotropy. This fact will make it relatively easy to design simple anisotropic structures that are optically equivalent to experimentally measured ones. Coatings of this type are useful for angular, spectral or polarization selectivity.

Thirdly, having explored single-material structures that are either random isotropic (sponges) or pseudo-random anisotropic (columnar), I turn to the problem of heterogeneous systems. The prototypical example is a paint-like coating in which some phases are randomly distributed inside a light-absorbing matrix. I will present a *generalized four-flux method* which is capable of analysing the optical response of realistic heterogeneous matrices. My new methodology is capable of dealing with factors including different size distribution of components, heterogeneous mix of materials, and weak absorption by the matrix (binder). A matrix formalism is developed to extend this method to multi-layer systems. The methodology is applied to the optimization of paints for achieving solar efficiency and I find that multi-layer paints with larger particles in the outer layer offer better performance in the IR.

Finally, I use a variation of the *C-method* to examine the effect of surface roughness on optical properties. Surface roughness is present in any kind of coating, including any of those described above, and, depending on its scale size, the optical response can vary significantly as a function of angle and wavelength. I analyse the angular effects caused by changing the correlation length of a surface profile with a fixed groove depth, i.e. increasing the noise of the surface and the effective slope of the profile to determine the angular dispersion. The effect of roughness on the optical properties is exemplified by showing how it can control the perceived colour of a gold surface. I show that some tuning of optical properties is possible by this means. My findings include that a significant reduction on reflectance with short correlation length, and that angular colour dependence of rough gold profiles shows a blue-white colour for s-polarization and a yellow-reddish colour for p-polarization.

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Author's Contributions

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List of Abbreviations

EMF	**E**lectro**M**agnetic **F**ield
EMA	**E**ffective **M**edium **A**pproximations
UV	**U**ltra**V**iolet
VIS	**VIS**ible
IR	**I**nfra**R**ed
NIR	**N**ear-**I**nfra**R**ed
MSP	**M**icro-**S**tructural **P**arameters
GRF	**G**aussian **R**andom **F**ield
LCGRF	**L**evel-**C**ut **G**aussian **R**andom **F**ield
BRDF	**B**idirectional **R**eflectance **D**istribution **F**unction

List of Symbols

$\vec{E}$	electric field	$\mathrm{V\,m^{-1}}$
$\vec{D}$	electric displacement field	$\mathrm{C\,m^{-2}}$
$\vec{B}$	magnetic inductance field	T
$\vec{H}$	magnetic field	$\mathrm{A\,m^{-1}}$
$\vec{P}$	polarization field	$\mathrm{C\,m^{-2}}$
$\vec{F}$	electric cavity field	$\mathrm{V\,m^{-1}}$
$\hat{\epsilon}$	permittivity tensor	$\mathrm{F\,m^{-1}}$
$\hat{\mu}$	permeability tensor	$\mathrm{H\,m^{-1}}$
$\hat{\alpha}$	polarizability tensor	$\mathrm{C\,m^{2}\,V^{-1}}$
χ	susceptibility	
$m = n + ik$	complex refractive index	
ω	angular frequency	$\mathrm{rad\,s^{-1}}$
c	speed of light	$\mathrm{m\,s^{-1}}$
λ	wavelength	m
Q_{ext}	extinction efficiency	
Q_{sca}	scattering efficiency	
Q_{abs}	absorption efficiency	
Q_{pha}	phase efficiency	
C_{ext}	extinction cross-section	$\mathrm{m^2}$
C_{sca}	scattering cross-section	$\mathrm{m^2}$
C_{abs}	absorption cross-section	$\mathrm{m^2}$
C_{pha}	phase cross-section	$\mathrm{m^2}$
$\hat{g}$	metric tensor	
η	number density	$\mathrm{m^{-3}}$
σ	standard deviation	

Chapter 3:

k	wavenumber	$\mathrm{m^{-1}}$
x	scale parameter	
a	effective radius	m

Chapter 4:

p_n	n-point probability function	
$K(\vec{r})$	kernel function	
β_{ji}	polarizability	$\mathrm{C\,m^2\,V^{-1}}$
ϕ	fill-factor	
d	system dimension	
k	wavenumber	$\mathrm{m^{-1}}$
$\mathcal{I}_i(\vec{r})$	indicator or occupancy function	
$\mathbb{G}$	Dyadic Green Tensor	
$\tilde{\mathbb{G}}$	Reduced Dyadic Green Tensor	
$\hat{a}_n$	system geometry tensor (permittivity series expansion)	
$\hat{\alpha}_n$	system geometry tensor (inverse permittivity series expansion)	
$\hat{A}_n$	Torquato's system geometry tensor (polarizability series expansion)	
$\mathbb{A}_n$	Monte Carlo system geometry tensor (polarizability series expansion)	
$\lfloor\cdot\rfloor_n$	$\mathrm{n^{th}}$ order lower bounds	
$\lceil\cdot\rceil_n$	$\mathrm{n^{th}}$ order upper bounds	
Υ_i	micro-structural parameters	

Chapter 5:

$n = n_1 + in_2$	complex refractive index	
k	absorption coefficient per unit length	$\mathrm{m^{-1}}$
s	scattering coefficient per unit length	$\mathrm{m^{-1}}$
ϵ	forward average path length	
β	backscattering ratio	
ζ	forward-scattering ratio	
K	total absorption coefficient per unit length	$\mathrm{m^{-1}}$
S	total scattering coefficient per unit length	$\mathrm{m^{-1}}$
$\tilde{\beta}$	average backscattering ratio	
$\tilde{\zeta}$	average forward-scattering ratio	
r	reflection coefficients	
R	total reflectance	
T	total transmittance	
ϕ	multi-layer transfer matrix	

μ_0	mean radius	m

Chapter 6:

$\vec{F}$	field parallel to the surface	$\mathrm{V\,m^{-1}}$ ($\mathrm{A\,m^{-1}}$)
$\vec{G}$	field parallel to the incidence plane	$\mathrm{A\,m^{-1}}$ ($\mathrm{V\,m^{-1}}$)
k	wavenumber	$\mathrm{m^{-1}}$
$\vec{S}$	Poynting vector	$\mathrm{W\,m^{-2}}$
ε	efficiency	
α_n	horizontal component of the wavenumber	$\mathrm{m^{-1}}$
β_n	vertical component of the wavenumber	$\mathrm{m^{-1}}$
K	grating number	
d	super-period	m
l_c	correlation length	m

To my family